BIOCORROSION NETWORK

A SUM-UP OF FIELD EXPERIENCES

TASK 2 CORROSION

- Avesta Sheffield AB, Sweden
- BASF, Germany
- British Steel plc, Swindon Technology centre, UK
- Denmark's Technical University, DTU, Denmark
- EDF, France
- Instituto per la Corrosione Marina, Italy
- Sintef, Norway
- Swedish Corrosion Institute, Sweden
- University of Portsmouth, UK

Introduction

- Carbon Steel in anaerob environments, field studies
- Low alloy steel and carbon steel in anaerob environments, laboratory studies
- Stainless steels anaerob environments, field and laboratory studies
- Stainless steels in aerob environments, field and laboratory studies
- Titanium, Nickel and 70Ni30Cu alloy

Carbon steel - Low water corrosion

- A statistical comparison between Normal Low Water Corrosion NLWC sites and Accelerated Low Water corrosion (ALWC) sites
- 22 sites in 39 visits where 10 were ALWC sites.

Acccelerated or Normal Low Water corrosion sites

- ALWC site
  - – Corrosion rates ~ 0.3 mm/y
  - – Local corrosion
  - – Corrosion products with poor adherence
- NLWC site
  - – Corrosion rates ~ 0.1 mm/y
  - – No local corrosion
  - – Adherent corrosion products

Statistical method used

- **Site ALCW is similar to NLWC**
- **Site ALCW is not similar to NLWC**

ALWC<NLWC **ALWC>NLWC**

Parameter comparison

- General environmental influences: Sunlight rates, mean water/air temperatures and geographical orientations: NLWC = ALWC
- The presence of high number of bacterias (SRB/SOB) did not correlate with low-water corrosion problems.
- No difference in the spatial distribution of bacteria in the layer close to steel surface between the sites.
- Sulphides were qualitatively detected on all sites.

Corrosion products

The number of culturable bacteria were everywhere lower in the innermost layer in contact with the steel.

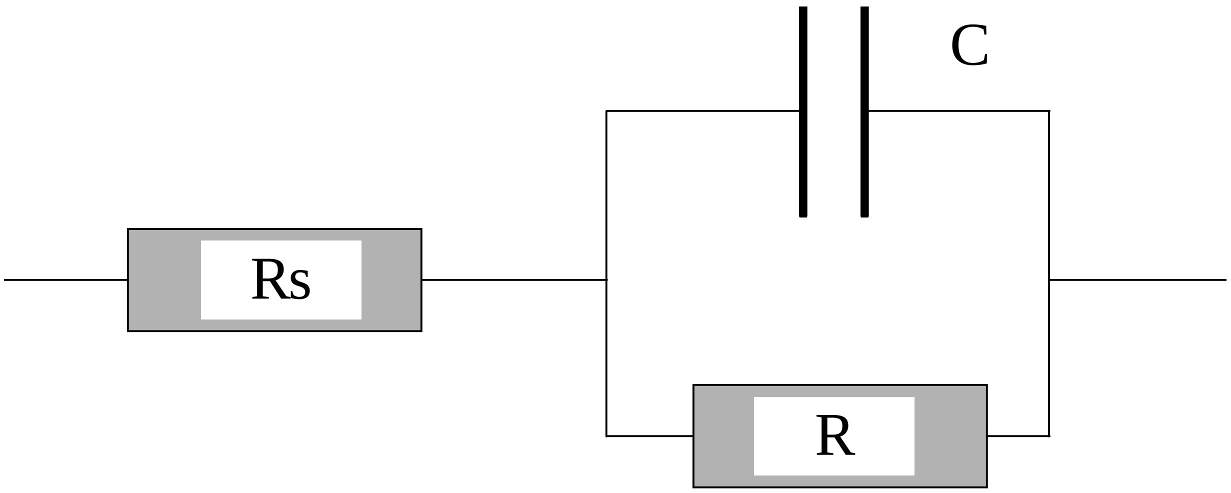
PARAMETER	ALWC	NLWC
ORGANIC MATTER	HIGHER	LOWER
ALGAE	HIGHER	LOWER
CHLORIDE	HIGHER	LOWER
HEAVY METALS	LOWER	HIGHER
PH	LOWER UNDERNEATH	HIGHER UNDERNEATH
PHOSPHORUS	LOWER	HIGHER

Statistical significant parameters related to ALWC

	ALWC	NLWC	One tailed t-test
Mean Tidal Range (m)	3.0 ± 2.1	4.9 ± 3.0	ALWC < NLWC P=0.047
- Data from Baltic Sea excluded	3.5 ± 2.1	5.3 ± 2.9	ALWC < NLWC P=0.075
Thickness of Corrosion Products (mm)	9.7 ± 6.4	6.1 ± 2.8	ALWC < NLWC P=0.016
pH undernaeath Corrosion Products	6.2 ± 0.7	6.8 ± 0.7	ALWC < NLWC P=0.021
Redox Potential of Seawater (mV vs. Ag/AgCl)	0 ± 106	54 ± 74	ALWC < NLWC P=0.05
Presence of Invertebrates	75%	93%	ALWC < NLWC P=0.07
Presence of Algae	90%	67%	ALWC < NLWC P=0.06
Organic Carbon (%)	2.2 ± 0.5	1.4 ± 0.5	ALWC < NLWC P=0.028
Organic Hydrogen (%)	1.2 ± 0.2	0.8 ± 0.2	ALWC < NLWC P=0.041
Organic Nitrogen (%)	0.36 ± 0.06	0.31 ± 0.02	ALWC < NLWC P=0.06
TOC of Seawater (mg l^{-1} O_2)	14.6 ± 13.5	7.2 ± 7.9	ALWC < NLWC P=0.036
MPN_{SOB} (Cells g^{-1} CP dry weight)	6.5 10^5 ± 2.1 10^6	3.5 10^3 ± 5.9 10^3	ALWC < NLWC P=0.08

Carbon steel - anaerob clay, bog - corrosion rates

- Measurements with a probe
- EIS- Electrochemical Impedance Spectroscopy
- Linear Polarisation Resistance measurements



Corrosion rates

Site, Denmark	Depth in clay	Exposure time	Rate EIS, µm/y	Weight loss, µm/y	Note
Vallensbæk, autumn, 2-12°C autumn	30 cm	6 months	200-400	10	bank, stream Cl- 240ppm
Utterslev, 5-15°C, spring	30 cm	6.5 months	5-10	30	bank, stream
Arresø bog late autumn	30 cm	47 days	init: 200 end: 10	5	marin sediment, stagnant
Kyndby, summer, 15 °C	70 cm	15 days	init: 145	20	SRB active mud, stagnant

Estimation of corrosion rates with EIS

- The equivalent circuit was not valid for all measurements, but this approach was taken to examine the general change in parameters.
- The risk of erroneous corrosion rate estimation was large especially if porosity was combined with a reactive film

Field tests in Denmark

- Corrosion rate could not be correctly assessed by EIS if sulphide was present
- DC-polarisation scans were very much effected by hysteresis and did not give a reliable corrosion rate
- Galvanostatic pulse measurements did not give reliable results

Cont. Field tests in Denmark

- Weight loss measurement was the most reliable technique, but it only gave accumulated corrosion rate.
- All techniques were sensible to the fact that the soil is heterogeneous and that the positioning of probe or weight loss coupons is critical.
- The most active SRB-environment Kyndby was at short time exposure not the most corrosive.

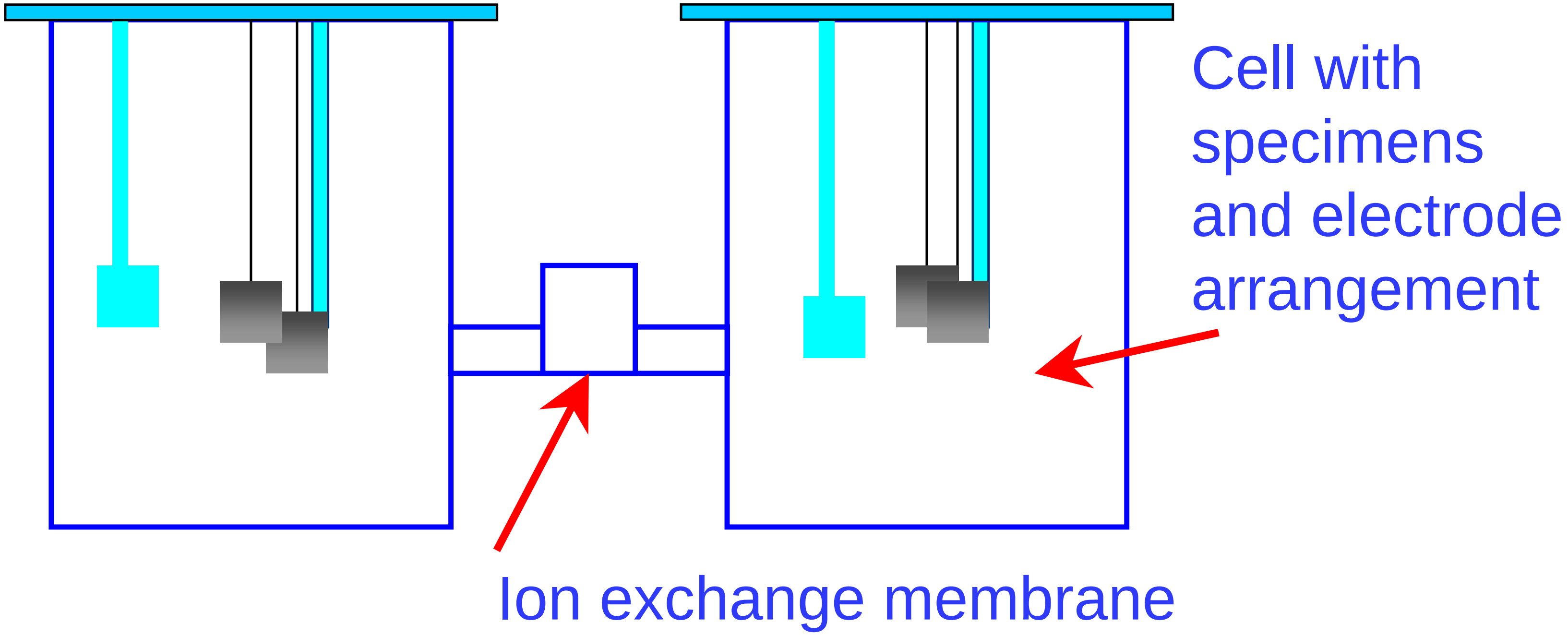
Low alloy steel and carbon steel - laboratory tests

- Material

Nominal composition	C	Si	Mn	P	S	Cr	Mo	Ni	Cu
1%Cr	0.066	0.27	0.95	0.005	0.005	1.02	<0.005	0.04	<0.02
2%Cr	0.081	0.24	0.93	0.006	0.005	1.96	0.006	0.06	<0.02
0.5%Mo	0.069	0.25	0.91	0.006	0.004	0.02	0.490	<0.02	<0.02
0.5%Cu	0.066	0.25	0.97	0.006	0.004	0.03	<0.005	0.04	0.51
1.85%Si 0.25Cr	0.060	1.85	1.04	0.014	0.004	0.25	-	-	-
1.35%Si 0.55%Cr	0.080	1.35	1.00	0.015	0.005	0.56	-	-	-
CrNiCu	0.057	0.43	0.74	0.012	0.005	0.90	-	0.23	0.29
Mild steel	0.110	0.04	0.53	0.012	0.007	0.02	-	0.02	<0.02

Experimental

- Dual cell arrangement
  - Filtered 0.2 µm Porthsmuth seawater
  - consortia COT, SOB, SRB to one of the cell



Results - low alloy steel and carbon steel, laboratory test

Steel grade	Corrosion rate (mm/y)	Comments
1% Cr	1.44	Inoculated
	0.04	Uninoculated
2% Cr	1.38	Inoculated
	0.39	Uninoculated, black deposits
0.5% Mo	1.59	Inoculated
	0.13	Uninoculated
0.5% Cu	1.06	Inoculated
	0.13	Uninoculated
1.8%Si, 0.25% Cr	1.40 (2.28)	Inoculated
	0.17 (0.16)	Uninoculated
CrCuNi	0.50 (1.02)	Inoculated
	0.13 (0.16)	Uninoculated
Mild steel	1.64	Inoculated
	0.08	Uninoculated

Low alloy steel cont.

- Inoculated cell
  - Black deposits, increased corrosion rates
- Uninoculated cell
  - Low corrosion rates

Biological drum reactor - laboratory tests

- Carbon steel AISI-SAE 1008
  - Three experiments, duration time: 70-120 days
  - 40 coupons, ø10 mm in a 120 dm^3 drum reactor containing artificial seawater (ASTM D1141-80) inoculated with SRB
  - Anaerob environment by Nitrogen gas purging
  - Inoculation with crude oil terminal SRB
  - Flow by rotation: 60 rpm
  - Temperature: 20-22°C
  - Chloride content: 17.7 ppm

Biological drum reactor, results

- General corrosion with a tendency to locality
- Initial corrosion rates determined with LPR and DC: 10 µm/y that increased to 2 mm/y after film formations
- Corrosion rates determined with EIS:
  - initial 10-100 µm/y
  - final 1-2.5 mm/y
- EIS: large capacitance as sulphide concentration increased
- OCP: -750 mV/SCE that increased after film formation to -650 mV/SCE

Stainless steels

- Anaerob environment
  - Seawater, clay
  - Wastewater treatment
- Aerob environment
  - Seawater
  - River water
  - Wastewater

Crevice corrosion resistance in anaerobic seawater

- Material: Stainless steelgrades, 1.4404 (316L), 1.4539 (904L), 1,4462 (2205), 1.4547 (254SMO) and 1.4652 (654SMO) with crevice formers of polyethylene
- Environment: Marine anaerobic bacteria SRB from a natural source fed with milk
  - Temperature: 30°C, pH 6.85-7.1
  - Sulphide: 320-500 ppm

Stainless steels and anaerob environment - seawater

- Electrochemical measurements: OCP, potentiodynamic polarisation scans (cathodic, anodic)
- Simulation of ennoblement in anaerobic environment corresponding to a coupled situation between anaerobic environment and aerobic environment (2mv/15 min)

Stainless steels - anaerob seawater, crevice corrosion

- OCP in anaerob environment ~ -550 mV/SCE
- No corrosion in a pure anaerobic environment
- Coupled situation in positive or negative direction can give an increased risk for crevice corrosion

Stainless Steel - Seawater polluted with sulphide

- 1.4401(316), 1.4462 (2205), 1.4447 (254SMO),1.4652 (654SMO)
- Crevice samples simulating real flange situations.
- Exposure in a tank ($5m^3$) with recirculated seawater (30-40 dm^3/h) for 95 days.
- Addition of 1000 ppm Na_2S in the start of the test.

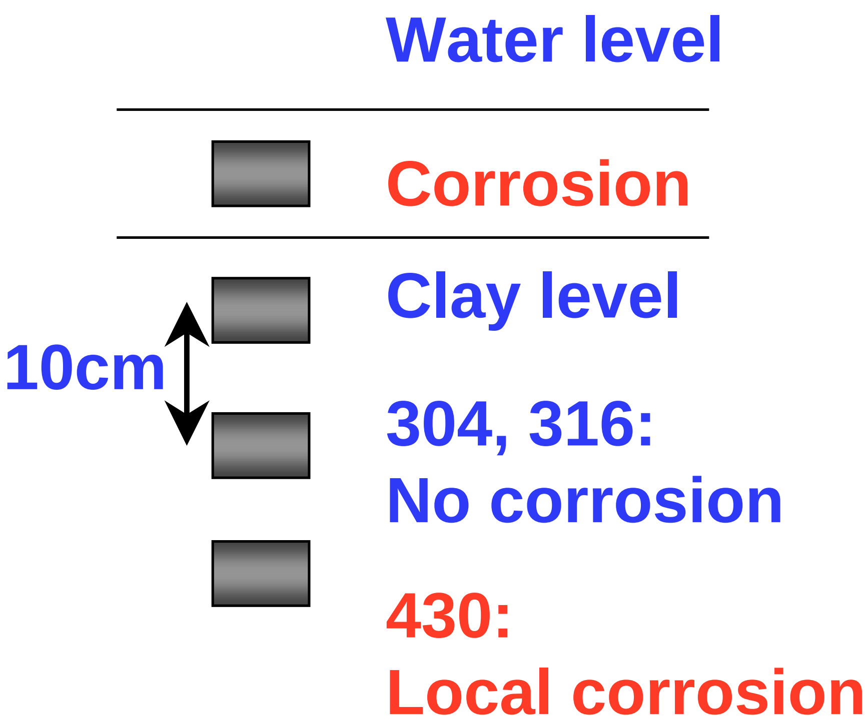
Results - SS in Seawater polluted with sulphide

- OCP ~ -515 mV/SCE,
- Redox ~ -500 mV/SCE
- Attacks on 1.4401 (316) at welds and at dark brown spots in the fusion line
- Pitting on 1.4401 (316) above the waterline

Chlorinated seawater

- 1.4401(316), 1.4462 (2205), 1.4447 (254SMO),1.4652 (654SMO) and nickel based alloys N06625, N10276
- Crevices simulating real flange situations
- Residual chlorine 7.7-13 ppm (~10 ppm)
- pH 8.0-8.1, Temperature 45°C
- No slime or biofouling after 95 days exposure
- Corrosion on all samples except 654SMO

Anaerobic clay environment in seawater at Genova harbour



- Stainless steel grades 1.4013(430) 1.4301(304) 1.4401(316)
- Exposure 6 months
- pH 7.6
- Sulphur content 2.65-3.15 mol/dm^3
- OCP: 304, 316 ~ -500
- OCP: 430 ~ -500 to -600

Stainless steels in aerob environment

- Seawater - MAST program - Biofilm project, Marine Biofilms on stainless steels, Effects, monitoring and prevention
- Fresh water and industrial system
  - River Rhine
  - Chemical plants
  - Wastewater
  - Nuclear Power Plants

MAST II

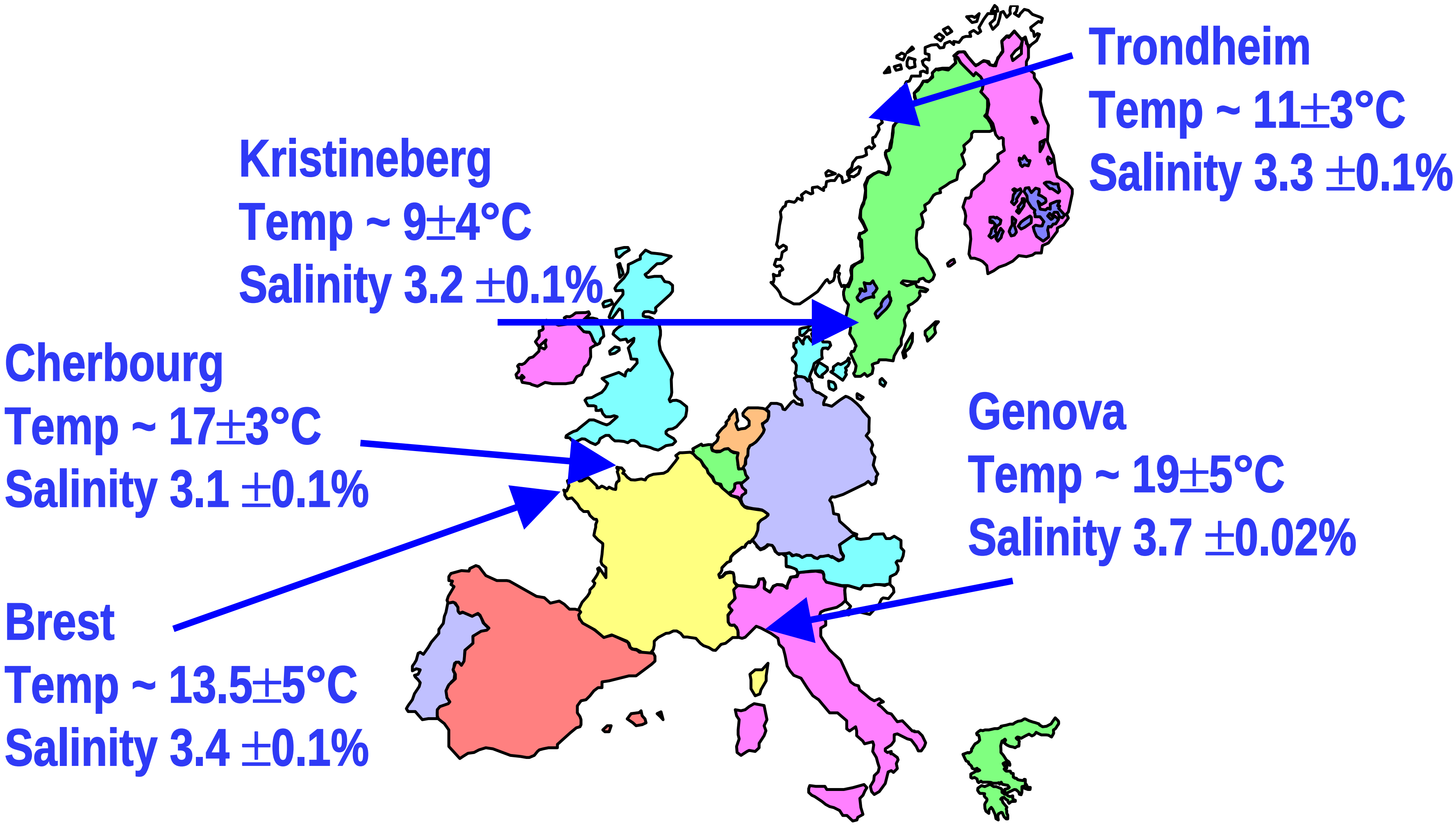
- Exposure in coastal seawaters in Europe with and without crevices (POM)
- Biofilm samples were collected to relate electrochemical effects to biofilm components

Table 1. Stainless steel grades exposed in the MAST II Program.

EN	Trade name	Chemical composition, (% weight)				
		Cr	Ni	Mo	Cu	N
1.4435	316L	17.2	12.6	2.6		
1.4462	2205	22	5.5	3.2		0.17
1.4460	UR47N	24.7	6.6	2.9		0.18
1.4507	UR52N+	25	6.3	3.6	1.5	0.25
1.4410	SAF 2507	24.9	6.9	3.8		0.28
1.4547	254SMO	19.9	17.8	6	0.69	0.2
1.4652	654SMO	24.5	21.8	7.3	0.43	0.48
1.4563	SAN28	26.7	30.3	3.4	0.9	0.07
1.4537	URSB8	24.9	25	4.72	1.4	0.21
1.4529	URB26	20	24.7	6.3	0.8	0.19

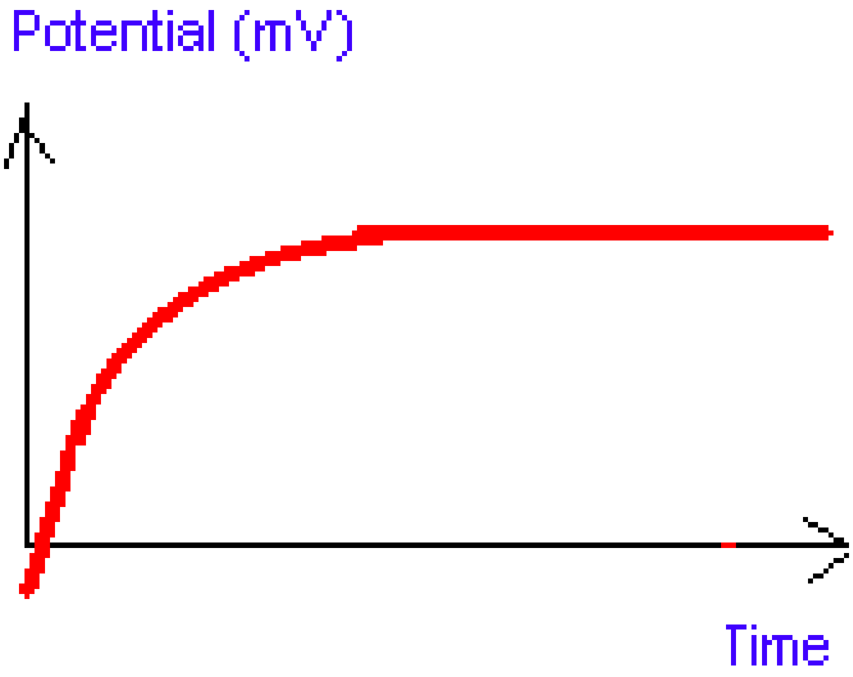
Geographical locations

- Exposure time : summer 93 - spring 94



Seawater exposure

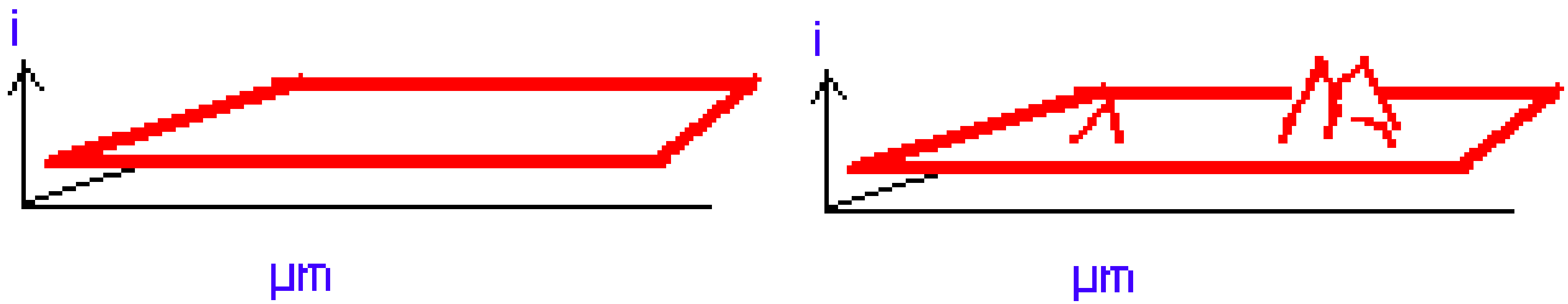
- Potential ennoblement and final value at all stations and seasons similar
- Initial OCP varied
- Incubation time varied with season



Seawater exposure, cont.

- No correlations with ennoblement:
  - pH
  - geographic location
  - stainless steel compositions
  - chlorphyll a
  - salinity
  - ash
  - organic matter contents, biomass
- Related to ennoblement:
  - Temperature
    - 20°C rapid increase of potential
    - 30°C rapid increase of potential
    - 40°C no ennoblement
  - EPS content (satisfactory correlation)

Biofilm growth and cathodic current evolution - SVET



- After one day of exposure, the oxygen reduction current was uniformly distributed over the whole stianless steel surface (1.4410, SAF2507)
- 50 days exposure in Baltic seawater in the laboratory showed preferential sites for a fast oxygen reduction
- By adding an enzymatic inhibitor the active sites were deactivated

Corrosion after exposure

- Crevice corrosion was found on 316 L exposed in Genoa, Italy and Trondheim, Norway
- The more alloyed steel grades either austenitic or duplex grades appeared to be resistant to crevice corrosion after 250 days (6000 hours) at all stations
- Depassivation (discolouration) appeared but there was no weight loss

MAST II - Experiences on real industrial components

- Cases of corrosion failures that occured in seawater systems at installations in the North Sea
  - Crevice corrosion in flanges
  - Treads with ciritical geometry for initiation
  - Improper surface treatment
  - Chlorinated systems on higher alloyed 6Mo Stainless Steel

Industrial systems

- Chemical plant using cooling water from River Rhine, 1.4401
  - Flow 1.5-2 m/s
  - Cl^- ~ 50-200 ppm,
  - Temperature 30-35°C
  - Pitting corrosion - pinhole leaks on welds
  - No corrosion on base material
  - Unpickled welds remaining heat tints
- Tubular heatexchanger - leaked after 5 years service 1.4462(2205) welded with (X2CrNiMoN17-13-5)
  - Temperature 30-50°C
  - Used for some weaks/year - often stagnant flow conditions dominated
  - River water remained in the tubes

Wastewater treatment

- Corrosion of SS 1.4404 (316L) pipes in a wastewater treatment plant after modernising with biological nitrification/denitrification unit; pharmaceutical plant
- 19 year corrosion free
- Six months after taking new unit into use:
  - Pitting at welded joints
  - Pitting nearly on nearly all circular welds
  - Pitting on base material but no leaks
  - Pitting and crevice corrosion on flanges and nozzles

Wastewater treatment, cont.

- Field tests in the final stages in four plants in Sweden for one year on 1.4301 (304), 1.4401 (316), 1.4462 (2205)
- Ennoblement: in two plants and with values close to the same as in seawater in one of the plants
- Corrosion was found on 1.4401(316) in one plant both on welds and base material
- Corrosion on 1.4301 (304)in three of the plants
- No corrosion on 1.4461 (2205)

Nuclear Power plant

- Fire protection system in a power plant and waste treatment system
- 1.4301 (304) 18-10 welded tubes
- 300-500 ppm chloride
- 100 ppm sulphate, pH 7.5-7.9
- Room temperature
- Leaks on the welds after one year

- Loop test with river water and sterilised water
- Enhanced corrosion in raw water loop
- Biofilm development on unpickled welds

Titanium, Nickel and 70Ni70Cu alloy - laboratory study

- Immersion in a tank of 100 dm^3 of natural seawater changed with renewal 100dm^3/h and in unchanged sterilised seawater, temperature: 25°C
- Ti: increase in the free corrosion potentials ~250mV/SCE in natural water
- Ni:Similar free corrosion potentials in natural and steril water but corrosion was found by weight loss
- 30Ni70Cu alloy: Similar free corrosion potentials in both environment but corrosion was found by weight loss

Conclusions

Discussion